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AMENDMENTS FOR THE CONTROL OF ACID MINE DRAINAGE

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MICROMEDIA

AMENDMENTS FOR THE CONTROL OF ACID MINE DRAINAGE

by

K.E. Haque*

ABSTRACT

This review provides a brief overview of the generation and controls of acid mine drainage (AMD) in the sulphidic tailing site. It also addresses the general approaches necessary for the selection of an amendment or a mixture of amendments for the mitigation of AMD in the sulphide tailings dump.

Keywords: Acid mine drainage, amendments, AMD control, sulphide tailings, acid generating tailings

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INTRODUCTION

When waste rocks or mine-mill tailings containing sulphide minerals are exposed to air and moisture they can undergo natural oxidation. This kind of oxidation often leads to the generation of acidic drainage containing sulphuric acid and a host of heavy metal cations. This phenomenon is often referred to as acid mine drainage (AMD) or acid rock drainage (ARD). Further, this oxidative acid generation/mineral dissolution process is enormously accelerated by the action of certain bacteria (e.g.; *thiobacillus ferrooxidans*) (1,2).

As the oxidation continues, the oxidation products (i.e., sulphuric acid and dissolved metal species) are flushed out of the tailing dam by rain water and/or snow-melt water. If the acidic stream is allowed to leave the tailing sites without any remedial treatment, then it contaminates ground water, local water courses and even the surrounding soils, and causes damaging effects in the ecosystems.

Currently, there are thousands of tailing sites in Canada covering almost 15,000 hectares with millions of tonnes of acid-generating sulphidic tailings from the base metals mine-mill operations alone, in addition to a large number of acid-generating tailing sites from gold, coal, and uranium mine-mill operations (2). In fact, AMD is a general problem for almost all of the mine-mill operations. Recently, as public concern over environmental issues grows, the industries are now more eager than before to find a long term remedial action for the problem of AMD.

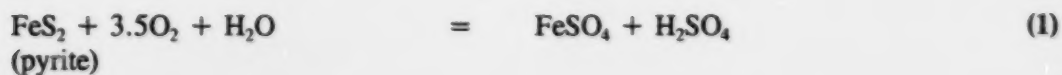
This review focuses on the basic chemistry of the generation of acid mine drainage and of AMD control by applying amendments with the tailings. An ideal amendment should have properties to neutralize the excess acid, precipitate metal ions from AMD, and form a hardpan (i.e., non-reactive solid barrier) between the oxidation (i.e., acid-generating zone) and reduction zones (i.e., unoxidized tailings). In these respects the oxides, hydroxides and carbonates of alkali (i.e., Li, Na, K, etc.) and alkaline earth metals (i.e., Mg, Ca, Sr, Ba), and aluminum are all suitable amendments. In addition to these, the carbonates,

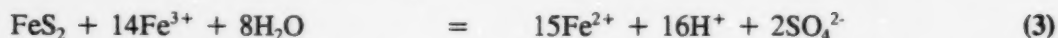
hydroxide/hydrated oxides of various heavy metals; and phosphates, silicates or clay minerals also function as an amendment for the control of AMD (1,3,4).

Chemistry of AMD Generation

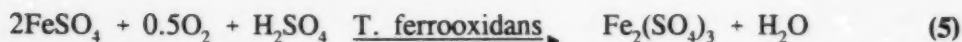
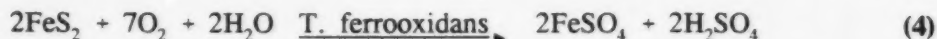
The vast majority of waste rocks and mill tailings contain various types of iron sulphides; the most common of which are pyrite (FeS_2), marcasite (FeS_2) and pyrrhotite (Fe_{1-x}S). Other sulphides such as chalcopyrite (CuFeS_2), arsenopyrite (FeAsS), molybdenite (MoS_2), galena (PbS), stibnite (Sb_2S_3), sphalerite (ZnS), cobaltite (CoAsS), pentlandite ($[(\text{Fe},\text{Ni})_9\text{S}_8]$), tetrahedrite [$\text{Cu}_{12}(\text{SbAs})_4\text{S}_{13}$] etc. may also be present in the waste rocks and mill tailings, but often as minors (1). These minerals may not contribute significantly to the generation of acid but they have a major contribution to the heavy metals content and toxicity of the AMD. In this context it is worth mentioning that waste rocks and mill tailings often contain acid-neutralizing minerals such as calcite (CaCO_3), dolomite [$\text{CaMg}(\text{CO}_3)_2$], siderite (FeCO_3), magnesite (MgCO_3), ankerite [$\text{CaFe}(\text{CO}_3)_2$], olivine [$(\text{MgFe})\text{SiO}_4$] etc. (1,3,4). In a strict sense, the AMD is a net effect of acid generation and acid neutralization in the tailing dump.

Generally, the acidity of tailings at the time of disposal is adjusted at or above neutral pH. At this pH condition bacterial oxidation of the sulphides is virtually non-existent. When the sulphides are exposed to air (i.e., oxygen) and moisture they usually undergo slow chemical oxidation with the formation of sulphuric acid and metal sulphates. For example, when pyrite undergoes this kind of oxidation, the initial products are sulphuric acid and ferrous sulphate (Eq. 1). As the acidic conditions increase and prevail in the oxidation zone, ferrous iron undergoes further oxidation into ferric iron with the oxygen from air or water (Eq. 2). Ferric ion itself is a strong oxidant and causes further dissolution of pyrite and other reactive minerals (Eq. 3) (1,6-10).





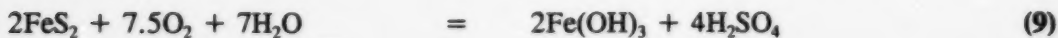
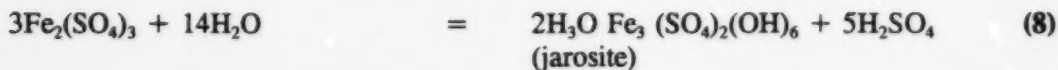
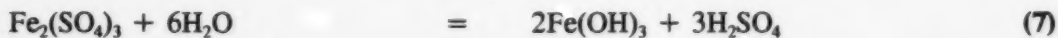
As pH in the oxidation zone reaches the range of 2-3, the oxidation of pyrite is further accelerated (10^3 - 10^6 orders of magnitude over the chemical oxidation rate) by the action of thiobacillus ferrooxidans. The same bacteria rapidly oxidize ferrous ion into the ferric state as long as oxygen is available. Equations 4 and 5 show typical bacterial oxidation products of pyrite (8-11).



The combination of reactions (1) and (2) or (4) and (5) is represented by Eq. 6, which indicates that each mole of pyrite oxidized generates 0.5 mole of acid and two moles of sulphate.

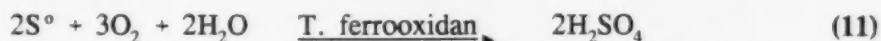
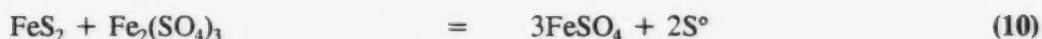


When pH in the oxidation/dissolution zone increases, ferric ion starts to precipitate as ferric hydroxide and/or jarosite with the generation of sulphuric acid (Eq. 7 and 8). In fact two moles of sulphuric acid are generated from one mole of pyrite (Eq. 9) (combination of Eq. 6 and 7).



The acidity, temperature and oxidation potential are all controlling factors for the type of oxidation products formed. For example, ferric ion would oxidize pyrite into ferrous

sulphate and sulphuric acid (Eq. 3) when the ferric ion concentration is in large excess; otherwise elemental sulphur would be formed (Eq. 10). However, elemental sulphur is easily oxidized into sulphuric acid by thiobacillus ferrooxidans (Eq. 11) (11,14-20).



So far the generation of acid mine drainage has been exemplified by oxidation/dissolution of pyrite. Essentially, all the sulphide minerals can undergo chemical or bacterial oxidation. Generally the bacterial oxidation rate is much faster than the chemical oxidation rate provided the oxidation conditions remain at pH 2-3; 20°C to 35°C, and an ample supply of oxygen is available. The following reactions (Eq. 12-17) show bacterial oxidation of some typical sulphides (1,11,12,14-17):



The bacterial oxidation of sulphides is largely responsible for the generation of AMD. The high bacterial growth depends not only on the availability of sulphides but also on a

sufficient supply of oxygen and on optimum acidity (pH 2-3) and temperature 20° to 35°C (in the oxidation zone). The water seepage through the tailing dump removes oxidation products from the oxidation/dissolution zone; while rain and/or snow-melt water accelerate the seepage flow. Oxygen is being supplied by diffusion of air and/or water seepage through the tailing dump.

Generally, the diffusion of air and moisture through a typical tailing dump is limited to the top layer of 1-3 ft. Therefore, the maximum oxidation/dissolution reactions take place in the top 1-3 ft. layer of the tailing dump. This layer is usually designated as the oxidation zone; whereas tailings below this layer are referred to as the reduction zone. As the acidic solution from the oxidation zone percolates through the tailing piles, a depletion in acidity and oxidation/reduction potential takes place. As a result, heavy metal cations begin to precipitate in varieties of mineralizations with the eventual formation of a non-reactive barrier (i.e., hardpan) between the oxidation and reduction zones. In effect hardpan formation prevents the diffusion of gaseous oxygen and the seepage of acidic water. Figure 1 is a simplistic representation of hardpan formation in the tailing dump (18).

It is clear from the foregoing discussion that oxygen and moisture are the two key reagents for the generation of AMD in the sulphidic tailings. Therefore, the exclusion of air (i.e., oxygen) or moisture from the sulphidic tailings would prevent AMD. It has been suggested by many authors that the exclusion of oxygen from reactive wastes would probably be the most effective long term control option for AMD (1). The control of AMD generation by covering of sulphidic tailing dump with water, clay, sand, tills, peat bogs, synthetic materials or combinations of these materials has been studied in laboratory and pilot scale tests and in some field applications (1,2,5,6,22-25). The generation of AMD could also be prevented by disposing of the sulphidic tailings in the permafrost region (1). Furthermore, AMD problems could be eliminated by removing sulphide minerals from the tailing by flotation (1). Apart from these preventive scenarios, the generation of AMD could be controlled by the application of a suitable chemical amendment or combination of amendments at certain points in the tailing dump (1,2,18,22,23,28).

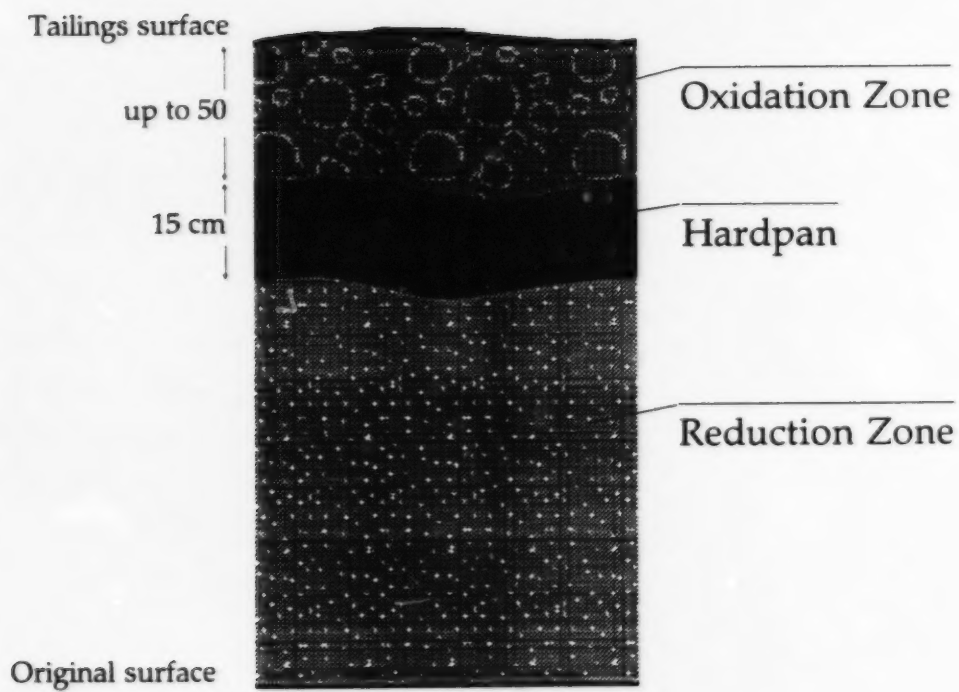


Figure 1. Different zones of a mine tailing dump.

The Chemical Roles of Amendments

The acidity of AMD is a major cause of dissolution and disposition of heavy metals species. When acidity decreases (i.e., pH rises) through neutralization processes, the precipitation of dissolved metals begins. However, there are some metals whose solubility actually increases with the rise in pH (e.g.; Zn Al). Table 1 shows a list of some common amendments. The neutralization and precipitation processes often lead to the formation of hardpan which is generally favoured with the precipitation of sulphates, hydroxides, hydrated oxides, silicates, phosphates and arsenates of various heavy metals.

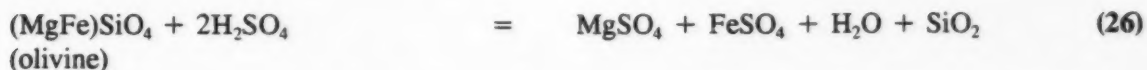
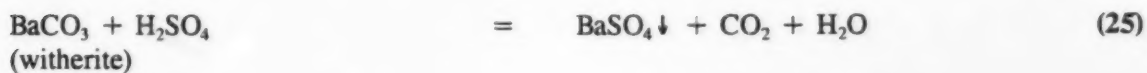
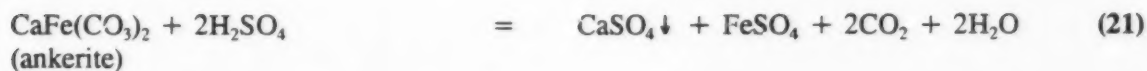
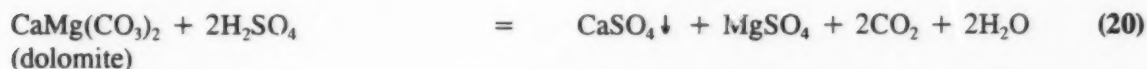
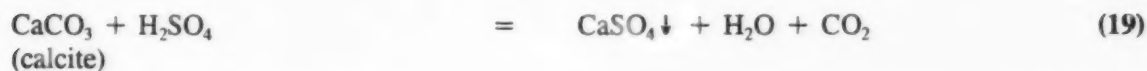
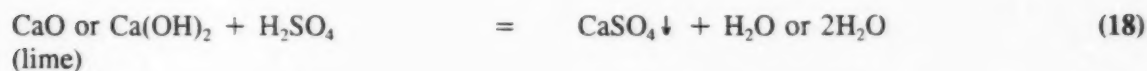
Table 1 - Amendments and their Neutralizing Potential

Materials/Minerals	Composition	Acid Consuming Potential ^(a)
Lime	CaO, Ca(OH) ₂	56, 74
Calcite	CaCO ₃	100
Dolomite	CaMg(CO ₃) ₂	92
Magnesite	MgCO ₃	84
Witherite	BaCO ₃	196
Gibbsite	Al(OH) ₃	26
Brucite	Mg(OH) ₂	29
Olivine	(Mg,Fe)SiO ₄	-
Apatite	Ca ₅ (PO ₄) ₃ (OH,F,Cl)	-
Ankerite	CaFe(CO ₃) ₂	108
Kaolinite	AlSi ₄ O ₁₀ (OH) ₆	-
Goethite	FeOOH	89

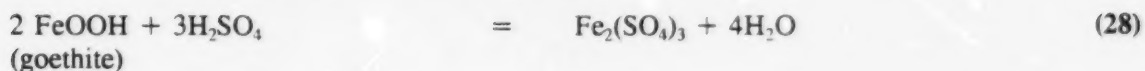
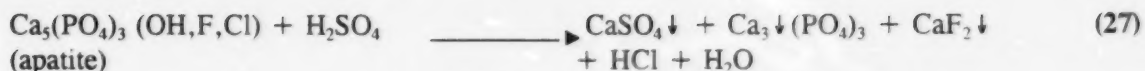
- (a) Acid consuming potential is the weight of the mineral required to have the same neutralizing effect as 100.0 g of calcite (CaCO₃). For example, the molar wt. of magnesite is 84.0 g and the molar weight of calcite is 100.0 g. Therefore, 84.0 g of magnesite supply the same amount of alkalinity as 100.0 g of calcite.

Sulphuric acid is the principal acidic component of AMD. During neutralization reactions with the added amendments metal sulphates are invariably formed. As a result, the

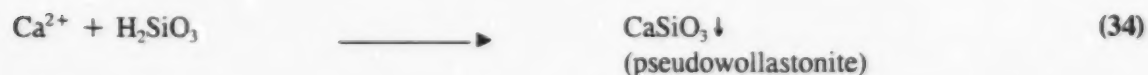
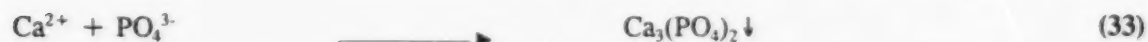
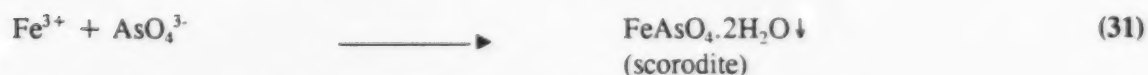
acid-neutralizing capacity of the amendments and the acid-generating potential of the sulphides are diminished considerably. If a suitable amendment could be mixed with the acid-generating sulphide tailings intimately and quantitatively with respect to acid generation potential, then the generation of AMD might be controlled. However, the particle size of the amendments is an important factor for efficient neutralization of the acid and precipitation of dissolved metals; in fact, the finer the particle, the greater the efficiency (3). This kind of measure could be applied in the uppermost 1-3 ft. layer of the tailing dump (i.e., oxidation zone). The following chemical reactions represent very simplistic mechanisms for neutralization and precipitation with various kinds of amendments:



↓ indicates precipitation



The above reactions represent some neutralization/precipitation mechanisms of sulphuric acid with various amendments. However, a number of heavy metals such as Fe, Cu, Pb, Co, Ni, Mo, Mn, Hg etc., may also precipitate as arsenates, hydroxide, sulphates, phosphates or silicates in single or mixed salt composition. Generally, the silicates, phosphates, and hydroxides of most of the heavy metals do not precipitate in good crystalline form. These kinds of precipitates are voluminous, but undergo dehydration during the mineralization process. In fact these kinds of precipitates have strong tendency to form a hardpan between the oxidation and reduction zones in the tailings dump. The following partial reactions show the formation of arsenate, phosphate and silicate with some metal cations:



The acid generation, precipitation and mineralization in the reactive tailings dump is a complex geochemical process. Even the degree of hydration of a metal salt may lead to the formation of a host of different kinds of minerals. Table 2 shows some of the iron sulphate minerals with varying degrees of hydration (19).

Table 2 - Minerals of Iron Sulphate with Variable Degree of Hydration (17)

Minerals	Chemical Formula
Melanterite	$\text{FeSO}_4, 7\text{H}_2\text{O}$
Ferricopiapite	$\text{Fe}_4(\text{SO}_4)_3(\text{OH})_2, 16\text{H}_2\text{O}$
Copiapite	$\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_4(\text{SO}_4)_6(\text{OH})_2, 20\text{H}_2\text{O}$
Romerite	$\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2(\text{SO}_4)_4, 14\text{H}_2\text{O}$
Kornelite	$\text{Fe}_2(\text{SO}_4)_3, 7\text{H}_2\text{O}$
Coquimbite	$\text{Fe}_2(\text{SO}_4)_3, 9\text{H}_2\text{O}$
Rhomoclase	$\text{H}_3\text{OFe}(\text{SO}_4)_2, 3\text{H}_2\text{O}$
Voltaite	$\text{K}_2\text{Fe}^{\text{II}}_5\text{Fe}^{\text{III}}_4(\text{SO}_4)_{12}, 18\text{H}_2\text{O}$
Halotrichite	$\text{Fe}^{\text{II}}\text{Al}_2(\text{SO}_4)_4, 22\text{H}_2\text{O}$
Jarosite	$(\text{H}_3\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$

The oxidation, dissolution, precipitation/mineralization reactions shown above are all over-simplifications of chemical changes actually taking place in the tailing dump. Therefore, prior knowledge of acid-generating minerals and of the net acid-generating potential of the tailings, penetration depth of gaseous reagents (i.e., O_2 , H_2O , CO_2) through the tailing piles and possibly a realistic prediction of heavy metal species and their concentrations in the AMD would lead to the selection and formulation of a suitable amendment or a mixture of amendments for effective control of acid mine drainage. It is further emphasized that maximum control measures should be applied in the oxidation zone (i.e. top 1-3 ft. layer) of the tailing dump.

Some Tips for Conducting AMD Control Tests with Amendments

1. Thorough analyses for the tailings should be obtained, in terms of acid-generating and acid-neutralizing minerals.

2. The maximum and net acid-generating potential of the tailings should be determined.
3. Similar determinations are necessary for the amendments; especially for the natural amendments.
4. A realistic prediction for possible composition of AMD (especially for cations and anions other than SO_4^{2-}) is beneficial in the selection of the kind of amendment.
5. Size optimization is necessary to obtain the best performance of an amendment; otherwise -10 mesh is a generally acceptable size.
6. For hardpan formation a layer of an amendment or a mixture of amendment should be placed preferably towards the lower end of the oxidation zone (i.e.; approximately 1.5-2.0 ft. below the tailing surface).

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